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Boron centres allow design, control and systematic tuning of neutral homoaromatics for functionalization purposes

James D. Mattock,[a] and Alfredo Vargas*[a]

Abstract: Homoaromatic compounds are currently viewed more as an interesting novelty with little to no practical application. Based on calculations within density functional theory, we show that the unique charge redirection properties of tricoordinate boron, along with it being isolobal to a carbocation allow for a larger range of two-electron donors to be utilized, leading to the rational design of homoaromatic compounds better suited to functionalization. Among others, these compounds show a strong dependency on the relative positioning of the hetero-atoms within the ring system, a modulation control rendered possible by the insertion of the boron centres.

Introduction

Homoaromatic compounds, i.e. compounds that feature a contiguous π-system with a non-contiguous σ-system, have been known for decades.[1] However such compounds are limited in scope and are generally highly charged. Density functional theory (DFT),[2] which has proven to be a versatile and convenient computational method offers an opportunity to screen large numbers of candidates in order to assess the basic principles of the construction of these compounds without the high (manpower and material) costs and with far easier control over structural isomerism and ultimately molecular design than traditional chemical synthesis. It was shown in previous work that computationally stable homoaromatic molecules can be designed via the use of carbenes[3] as two-electron donors within homotropylium and norbornyl analogues and a set of metrics for assessing the strength of homoaromaticity was proposed.[4] However, in order to maintain a significant delocalized π-cloud in the majority of the homoaromatic candidates it was found that a carbocation was required to act as an electron acceptor. This requirement for the carbocation renders it impossible to design neutral homoaromatic systems. It was also found that due to the transient nature of a positive charge within a conjugated system the carbocation would migrate to the position adjacent to the carbene. The element boron is an ideal tool to combat these issues due to its unique properties which allow it to act as an electron 'sink'. Its ability to accept and donate charge and the fact that a tricoordinate boron atom is isolobal with a carbocation should allow for the acceptance of electron density from the carbene and its subsequent incorporation into the delocalized π-system. The ability of tricoordinate boron to mimic a carbocation and facilitate a homoconjugative interaction has previously appeared in literature.[5] The use of boron allows for control over the structural isomers thus allowing for a broader scope of design. The following sets of molecules are based on homotropylium analogues using either an N-heterocyclic carbene or bent allene[6] as the two-electron donor. Here, the objective is not necessarily to obtain the best example of a homoaromatic system, rather it is to acquire a measure of control over the strength of aromaticity within a molecule via the use of the structural isomers resulting from the relative arrangement of the two-electron donor, the electron acceptor, the sp^3 centre and the conjugated system.

The unique features of boron being its electron deficiency and its ability to act as an electron 'reservoir'[7] may also open up other avenues for the design of homoaromatic systems. Whilst it has been shown that carbenes offer a strong enough source of electron donation to stabilize a homoaromatic interaction, they are also a source of significant additional steric bulk thus incurring further complexity in attempts to functionalize homoaromatic compounds. Therefore sets of molecules have also been investigated that simply use a nitrogen atom within the ring as a two-electron donor in conjunction with a boron atom with the aim of generating a homoaromatic system with a greater utility for functionalization. A similar set of structural isomers has been characterized in order to again assess whether these compounds offer a route to the controllable modulation of the strength of aromaticity. The set of metrics for homoaromaticity as defined in a previous work will be applied in order to assess trends in the set of designed candidates. However, given that the aim of this work is to achieve a significant amount of electron donation into the vacant p_z orbital on a boron atom an additional metric for homoaromaticity is required; the boron centres should adhere to sp^2 geometry as the vacant p_z orbital should be aligned with the delocalized π-system. Additionally, calculations have been performed to assess additional routes towards the functionalization of the systems via the addition of hetero atoms within the homoaromatic ring.

Results and Discussion

Relying on a carbocation to provide the properties of a base building block can significantly convolute compound design given its large concentration of electron density and its attendant steric bulk. Given the isolobality of boron with a carbocation, and borons documented ability to act as an electron 'sink', this element would seem the obvious choice to allow for the removal of carbocations, however the insertion of a heteroatom within a ring system increases the number of possible structural isomers

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which may well exhibit differing properties, thus a range of structural isomers have been evaluated.

The assessment of structural isomerism across multiple variations obviously requires the analysis of large numbers of compound variations; thus the schematic shown in Figure 1 will be used as the basis for a naming convention, 7-N(#)B(#)I(#)A(#) where the first number denotes ring size and the positions of two-electron (i.e. amine-type) nitrogen donors (N), boron atoms (B), carbons with an attached carbene (I) and one-electron (i.e. imine-type) nitrogen donors (A) are denoted by the number following in parentheses.

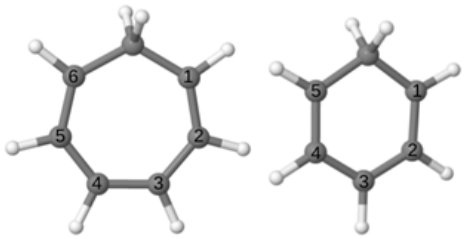

Figure 1. Schematic of the numbering system used to enable the specification of the positions of heteroatoms.

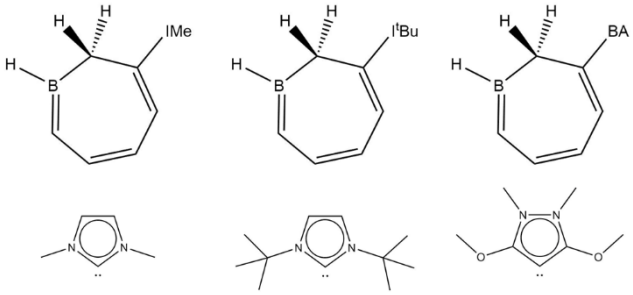

Figure 2. The homoaromatic compound 7-B(6)I(1) is shown here with the two-electron donors used, left to right; the N-heterocyclic carbenes IMe and I^{t}Bu along with a bent allene (BA)..

The resultant evaluation of the properties of boron and carbene including homoaromatic candidates is shown below in Table 1.

As in previous work the addition of steric bulk, i.e. exchanging IMe for I^{t}Bu (as shown in Figure 2) and adding methyl groups to the adjacent carbon atoms, in order to prevent the quinoidization of the carbene tends to provide stronger homoaromatic interactions among the candidates, as does the replacement of the carbene with a bent allene to decrease π-donation back onto the donating group. The data shown in Table 1 corresponds to the candidates with added bulk due to the rearrangement of 7-B(2)I(3) when optimized with IMe. A comprehensive list of results is given in the ESI. It is immediately evident that there exists a significant range of the strength of the homoaromatic interaction across the differing structural isomers. Despite the increase in degree of aromaticity, the trend among the structural isomers is largely maintained. That is, the homoaromaticity seems at its strongest when the boron-carbene interaction bridges the homoconjugative gap. Unsurprisingly, bond length deviation between structural isomers is slight, but some decrease in the size of the homoconjugative gap can be seen with an increase in homaromatic character. The presence of appreciable bond orders across the homoconjugative gap and negative $NICS_0$ values suggests the majority of the structural isomers show homoaromatic character. However, the equalization of bond orders, bond length and ^{13}C shifts is lacking. This is likely due to the introduction of the heteroatom into the ring. It should be noted that the torsion angles indicate only slight quinoidization of the carbene however quinoidization is heavily present in the IMe candidates (ESI).

Table 2 shows data for the six-membered rings where the boron atom acts to both donate an electron to the π-system and to partially accept the pair of electrons provided by the carbene. This should be possible as a result of borons apparent capability to act as a charge redirection node. In this case the set of data using bent allenes in place of the carbene is shown due to the rearrangement of some of the candidates with the other data sets, likely due to an excessive acceptance of electron density by the boron centre. Here, the six-membered rings seem to show a greater magnitude of interaction across the homoconjugative gap than that of similar seven-membered compounds. However, in cases such as 6-B(2)I(3) and 6-B(3)(1), where the majority of the metrics of homoaromaticity suggest the likelihood of only a weak homoaromatic system there is still a

Table 1. Calculated indicators of aromaticity for seven-membered, boron-substituted, structural isomers with a carbene donor including additional steric bulk. Inter-ring torsion angles are between N_{carb}-C_{carb}-C-C (in º). Chemical shifts of carbene-bound carbon nuclei are shown in ppm.

Compound identifier	WBI of the homo-conjugative gap	Inter-ring torsion angles	Homoconjugative gap distance	δ(^{13}C) in the π-system	δ(^{13}C) of C_{carb}	δ(^{1}H) upon C in the π-system	δ(^{11}B)	$NICS_0$
7-B(4)I(3)	0.05	96.3 / 102.0	2.48	102, 147, 107, 135, 143	175	6.14, 6.03, 4.71	40	-1.77
7-B(6)I(1)	0.13	-82.7 / -87.1	2.49	92, 141, 113, 148, 121	164	5.75, 7.32, 6.00	32	-5.61
7-B(2)I(1)	0.09	80.8 / 75.3	2.46	147, 120, 128, 119, 100	175	5.86, 6.06, 5.24	35	-4.50
7-B(1)I(2)	0.06	-89.4 / -93.0	2.53	154, 140, 132, 145, 102	174	6.85, 5.44, 6.13, 6.69	34	0.02
7-B(2)I(3)	0.13	100.3 / 88.3	2.39	146, 124, 118, 106, 144	173	4.34, 5.74, 5.23	29	-4.92
7-B(4)I(1)	0.06	-95.1 / -86.3	2.52	157, 120, 147, 141, 81	165	5.63, 6.74, 5.58	36	-1.96

significant $NICS_0$ value suggesting that some perturbation of the $NICS_0$ value is incurred due to the reduced size of the surrounding sigma-bond system. Thus $NICS_0$ may be insufficient as metric by its own merits. A highly conjugated system appears to be exhibiting a large $NICS_0$ value without necessarily possessing aromaticity, whilst this appears to be contrary to previous literature, it seems possible that a non-continuous sigma system may reduce the $NICS_\sigma$ component resulting in an artificially negative NICS value.[8]
Thus it is necessary to examine the bond order across the gap in the sigma system as well as the symmetry around the individual atoms as a system where the boron accepts more electron density may not result in a stronger homoaromatic interaction. Despite their synthetic accessibility, there are experimental difficulties inherent in incorporating carbenes, and thus instances of homoaromaticity, into larger systems. This is made more difficult by the need for additional bulk to prevent quinoidization. Thus, in order to allow for additional functionality the [C-carbene] fragments were substituted with isoelectronic [N-H] fragments within the ring. Here the greater propensity of boron to accept electron density should compensate for the decrease of donor strength.
Table 3 shows data with a [N-^{t}Bu] fragment as the donor as these compounds tend to show a greater degree of homoaromatic character. They again show significant bond orders and $NICS_0$ values across the homoconjugative gap and similar structural trends. There is a slight decrease in the strength of the homoaromatic interaction. However, contrary to

Table 2. Calculated indicators of aromaticity for six-membered, boron-substituted structural isomers with a bent allene donor. Ordered as per Table 1.

Compound identifier	WBI of the homo-conjugative gap	Inter-ring torsion angles	Homoconjugative gap distance	δ(^{13}C) in the π-system	δ(^{13}C) of C_{carb}	δ(^{1}H) upon C in the π-system	δ(^{11}B)	$NICS_0$
6-B(2)I(3)	0.01	-41.4 / -17.5	2.57	137, 124, 56, 60	115	6.14, 4.87, 3.21	75	-4.72
6-B(1)I(3)	0.14	-81.4 / -97.0	2.40	137, 115, 87, 42	111	5.05, 4.94, 4.54	109	-8.44
6-B(2)I(1)	0.02	-63.0 / -34.2	2.57	113, 148, 52, 58	120	2.18, 6.44, 4.26	77	-7.00
6-B(4)I(1)	0.03	-108.5, -100.8	2.56	44, 61, 157, 75	109	2.72, 6.12, 1.95	84	-4.78
6-B(3)I(1)	0.02	49.5 / 61.7	2.53	84, 142, 135, 43	120	8.01, 7.34, 8.38	163	-6.48
6-B(5)I(1)	0.21	-57.9 / -54.1	2.26	119, 94, 66, 52	112	4.02, 5.10, 3.93	85	-10.36
6-B(1)I(2)	0.17	-61.9 / -81.3	2.50	95, 132, 118, 90	108	3.22, 5.15, 5.82	102	-6.51

Table 3. Calculated indicators of aromaticity for seven-membered, boron-substituted, structural isomers where two-electron donation occurs from a [N-^{t}Bu] fragment within the ring. Chemical shifts are shown in ppm.

Compound identifier	WBI of the homo-conjugative gap	Homoconjugative gap distance	δ(^{13}C) in the π-system	δ(^{15}N) of N	δ(^{1}H) upon C in the π-system	δ(^{11}B)	$NICS_0$
7-N(2)B(1)	0.09	2.43	138, 121, 128, 125	206	5.62, 6.18, 6.09, 6.84	26	-5.10
7-N(1)B(2)	0.04	2.47	134, 138, 146, 148	188	6.88, 7.05, 6.52, 5.92	32	-1.83
7-N(3)B(4)	0.03	2.47	138, 114, 150, 139	207	6.28, 6.60, 5.00, 6.36	34	-1.28
7-N(1)B(6)	0.09	2.49	142, 107, 155, 136	145	6.67, 5.43, 7.53, 6.81	37	-3.97
7-N(1)B(4)	0.04	2.48	155, 114, 152, 137	163	7.25, 5.50, 7.01, 6.13	45	-1.43
7-N(3)B(6)	0.12	2.31	100, 130, 143, 120	193	4.53, 6.43, 7.24, 6.00	35	-7.52

Table 4. Calculated indicators of aromaticity for six-membered, boron-substituted, structural isomers where two-electron donation occurs from a [N-H] fragment within the ring. Ordered as per Table 3.

Compound identifier	WBI of the homo-conjugative gap	Homoconjugative gap distance	δ(^{13}C) in the π-system	δ(^{15}N) of N	δ(^{1}H) upon C in the π-system	δ(^{11}B)	$NICS_0$
6-N(1)B(5)	0.06	2.27	122, 81, 50	130	4.78, 3.38, 2.67	124	-6.93
6-N(1)B(4)	0.03	2.50	156, 82, 87	119	6.41, 3.64, 2.35	52	-4.78
6-N(1)B(3)	0.03	2.52	85, 125, 168	79	4.23, 5.61, 6.72	79	-4.34
6-N(1)B(2)	0.02	2.51	40, 145, 114	89	2.07, 6.64, 4.61	75	-7.64
6-N(3)B(5)	0.12	2.22	117, 136, 89	85	5.52, 5.62, 5.47	132	-8.05
6-N(3)B(4)	0.01	2.56	130, 139, 44	107	5.23, 6.03, 2.14	67	-5.28
6-N(2)B(1)	0.37	2.47	121,127,68	161	5.33, 6.04, 2.69	61	-10.18

the carbene-stabilized compounds, the strongest interactions appear to occur when only the boron atom is adjacent to the homoconjugative gap. This suggests that the unique electron acceptor properties of boron can allow for the formation of homoaromatic compounds using nitrogen as a two-electron donor whilst remaining a neutral compound.

Table 4 shows data for the six-membered rings in order to again evaluate boron both donating an electron to the π-system and to partially accept the pair of electrons and pertains to the unsubstituted nitrogen data despite showing a lesser degree of homoaromaticity, due to the rearrangement of one of the ^{t}Bu substituted nitrogen structural isomers. These show a similar general increase in interaction across the homoconjugative gap as seen in the carbene-based compounds upon the reduction of the ring size and a similar broad increase in $NICS_0$ values. They again show significant interactions across the homoconjugative gap but to a lesser extent than the comparable carbene-based analogues. They also possess similar positional trends to the seven-membered variants. Given the increased potential for functionality gained from the replacement of carbenes and the inclusion of boron centres this was expanded by introducing an additional unsubstituted nitrogen atom into the ring system as a single electron donor to the homoaromatic system and thus leaving its lone pair available for chemical applications i.e. the creation of pyridene-like analogues. The numerical metrics related to the strength of homoaromaticity upon the addition of an ancillary nitrogen atom to the seven-membered, nitrogen-donor-based aromatic system is displayed in Table 5. The data set constitutes a significantly larger analysis of structural isomers due to the larger number of distinct combinations possible. Thus there is an even greater range in the strength of the homoaromatic interaction across the isomers, however, upon assessment of the homoconjugative gap it can be seen that a number of the isomers show a significant bond order and a concurrent reduction in distance.

Despite these metrics, the nature of the through-space π-interaction is complex to portray accurately. In particular, as discussed earlier, the use of $NICS_0$ as a measure of aromaticity is a feature of much discussion.[9] It is generally agreed that a greater degree of accuracy and additional detail can be provided by the use, but not without flaw, of $NICS_{zz}$ values,[10] furthermore, this exact positioning of individual tensors is convoluted, in much the same way as the difficulty in positioning a ghost atom for $NICS_1$, with homoaromatic molecules which often do not possess exact planarity. Additionally the main flaw with $NICS_0$ values is the convolution of the isotropic shielding originating from the surrounding σ-system, thus, when used as a relative measure comparing the strength of aromaticity with a set of structural isomers this error should remain relatively constant. When used in conjunction with an electron localization method, $NICS_0$ can provide a useful indication as to the relative strength of aromaticity at a slight computational cost. Applying an electron localisation method to display the location of the bonding interactions, more specifically the delocalized ring system implicit in aromatic compounds is a powerful method to elucidate the nature of the homoconjugative gap. What is thus needed is a rigorous method of mapping electron density. Previously this would have been achieved using the Electron Localisation Function (ELF)[11] however this method, whilst useful, possesses several flaws.[12] The Single Exponential Decay Detector (SEDD), a more recent method designed by de Silva et al. is based solely on the density and is relatively computationally inexpensive and gives an accurate, qualitative image of the bonding interactions within molecules.[13] The relationship between SEDD at each point of a defined grid and the electron density ($\rho(\boldsymbol{r})$) is shown below in Equation 1:

Table 5. Calculated indicators of aromaticity for seven-membered, boron-substituted, structural isomers where two-electron donation occurs from a [N-H] fragment with additional steric bulk within the ring with a nitrogen one-electron donor (unsubstituted N atom) introduced into the ring. Ordered as per Table 3.

Compound identifier	WBI of the homo-conjugative gap	Homoconjugative gap distance	δ(^{13}C) in the π-system	δ(^{15}N) of N	δ(^{1}H) upon C in the π-system	δ(15N) of A	δ(^{11}B)	$NICS_0$
7-N(1)B(6)A(4)	0.15	2.34	177, 130, 126	136	9.45, 7.70, 6.09	453	24	-5.78
7-N(1)B(6)A(5)	0.06	2.43	142, 103, 160	153	8.36, 5.31, 6.86	362	17	-5.21
7-N(1)B(6)A(3)	0.07	2.49	131, 170, 151	177	7.46, 8.33, 7.94	289	42	-2.70
7-N(1)B(6)A(2)	0.16	2.31	147, 138, 135	181	7.36, 7.13, 7.46	395	25	-7.39
7-N(5)B(6)A(1)	0.07	2.47	142, 119, 159	214	6.82, 5.90, 7.94	394	32	-3.12
7-N(3)B(6)A(1)	0.06	2.43	119, 149, 144	208	5.90, 7.26, 7.31	326	48	-3.66
7-N(2)B(6)A(1)				Rearranged				
7-N(1)B(2)A(6)	0.03	2.44	155, 142, 168	206	8.29, 6.75, 7.06	409	30	-1.32
7-N(1)B(2)A(3)	0.03	2.48	167, 138, 145	180	8.91, 6.30, 6.15	428	27	-0.84
7-N(1)B(4)A(2)	0.06	2.45	148, 151, 136	213	7.59, 7.06, 6.04	453	40	-2.12
7-N(3)B(4)A(2)	0.04	2.45	143, 140, 141	264	6.85, 6.39, 6.33	393	30	-1.97
7-N(3)B(4)A(1)	0.03	2.45	153, 139, 155	222	6.36, 6.80, 7.52	329	34	-1.29
7-N(2)B(3)A(4)	0.21	2.26	121, 160, 78	229	5.55, 7.89, 4.01	314	18	-9.63
7-N(1)B(3)A(4)	0.07	2.42	165, 160, 93	237	6.62, 8.37, 4.40	367	25	-5.65

$$SEDD(\boldsymbol{r}) = \ln\left[1 + \left(\frac{\nabla\left(\frac{\nabla\rho(\boldsymbol{r})}{\rho(\boldsymbol{r})}\right)}{\rho(\boldsymbol{r})}\right)^2\right]$$

Equation 1: The definition of SEDD describing its relation to the electron density, $\rho(\boldsymbol{r})$.[13]

The current literature utilising SEDD applies the method to small, planar molecules and reproduces atomic shell structure with a good degree of accuracy, these are then applied, alongside isosurfaces, to define a 'fingerprint' of aromaticity.[14] Whilst the homoaromatic candidates are more complex, and often deviate significantly from planarity, by concentrating on the homoaromatic ring structure SEDD should provide a useful additional metric in the identification and classification of homoaromatic compounds. Whilst an SEDD analysis would be purely a qualitative analysis, it is a powerful tool in the identification of homoaromatic compounds which adds a strong additional metric to those previously established. In this work the SEDD diagrams display the values of the SEDD as a colour scale on a cut plane showing the largest degree of homoaromaticity. This should be a fully valid approach as aromatic orbitals should be planar. However, due to the strain introduced in the system by the addition of an sp^3 centre into the sp^2 system the homoaromatic rings tend to show a significant deviation away from planarity. To alleviate the impact of the non-planarity the cut contour has been placed such that it includes the plane through which a through-space interaction across the homoconjugative gap i.e. in the area in which some evidence of a bonding interaction would be expected. Figures 3 and 4 show contour planes and isosurfaces for a selection of homoaromatic candidates. The contour planes in figure 3 clearly show the atomic shell structure of those carbon atoms which it bisects. Also evident is the presence of the σ-system, it should be noted that the areas of seemingly low electron density in these bonds are caused by the deviation of these bonds away from the chosen cut plane. Literature states that the confirmation of aromaticity is the presence of a continuous ring of electron density within the centre of a molecule. These continuous rings do not appear in the candidates shown, this is not unexpected as homoaromaticity is known to be a weaker interaction than that of classical aromaticity. However, in the majority of compounds, there can be seen a continuous crescent of electron density where the σ-framework coincides with the π-system. The continuity of this crescent suggests aromaticity over mere conjugation. The difference arises in the area of the postulated through-space interaction. Here, instead of a section of continuous electron density there appears a single bead of electron density equidistant between the bridgehead carbon atoms of the π-system. It is apparent that whilst the crescents are continuous they are not homogeneous; this disparity is likely caused by the deviation of the homoaromatic molecule away from planarity. This variation within the crescent also yields an approximation of the relative strength of the homoaromaticity between the compounds upon direct comparison although not with a degree of accuracy sufficient to replace the previously discussed metrics. To ensure that the perceived indicators of aromatic character are not a fortuitous representation of a heavily conjugated system, the other 'fingerprint of aromaticity' suggested by de Silva et al. was also investigated. It is also important to recognise that, as stated in previous literature, the appearance of the continuous ring of electron density is also heavily dependent upon the geometry of the aromatic system. This is likely to be a particularly prevalent issue in homoaromatic compounds given the tendency of the homoaromatic interaction to deviate away from planarity due to the presence of the tetrahedral sp^3 centre. This perturbation to the geometry could cause the central ring of density to fragment and appear non-aromatic in nature; the same previous literature also suggests the isosurfaces as a way to mitigate this issue.

These isosurfaces show the single localisation domain that has been associated with aromaticity but, in a similar manner to the cut planes, it only appears where the σ-framework and the π-system coincide. Crucially, a portion of electron density is observed in the exact position where the bead of electron density is observed in the cut plane. This rules out a false positive being caused by the proximity of the sp^3 centre and thus confirms that there is some through-space interaction between the terminal carbon atoms. It should be noted that the generation of clear isosurfaces becomes increasingly difficult the size and the complexity of the compound increases as it becomes more difficult to prevent pertinent detail from being obscured. The contour planes and isosurfaces shown here were calculated using a ZORA-QZ4P STO basis set as these calculations provide a more precise image for both representations. The images generated from calculations utilising a TZ2P STO basis set do still yield useful information and may be worth considering for larger systems (TZ2P images are given in the SI). It should be noted that although literature shows that basis sets larger than QZ4P provide more precise mapping, the computational cost becomes prohibitive with larger molecules thus making, using a larger basis set, the method less attractive for use as a metric.

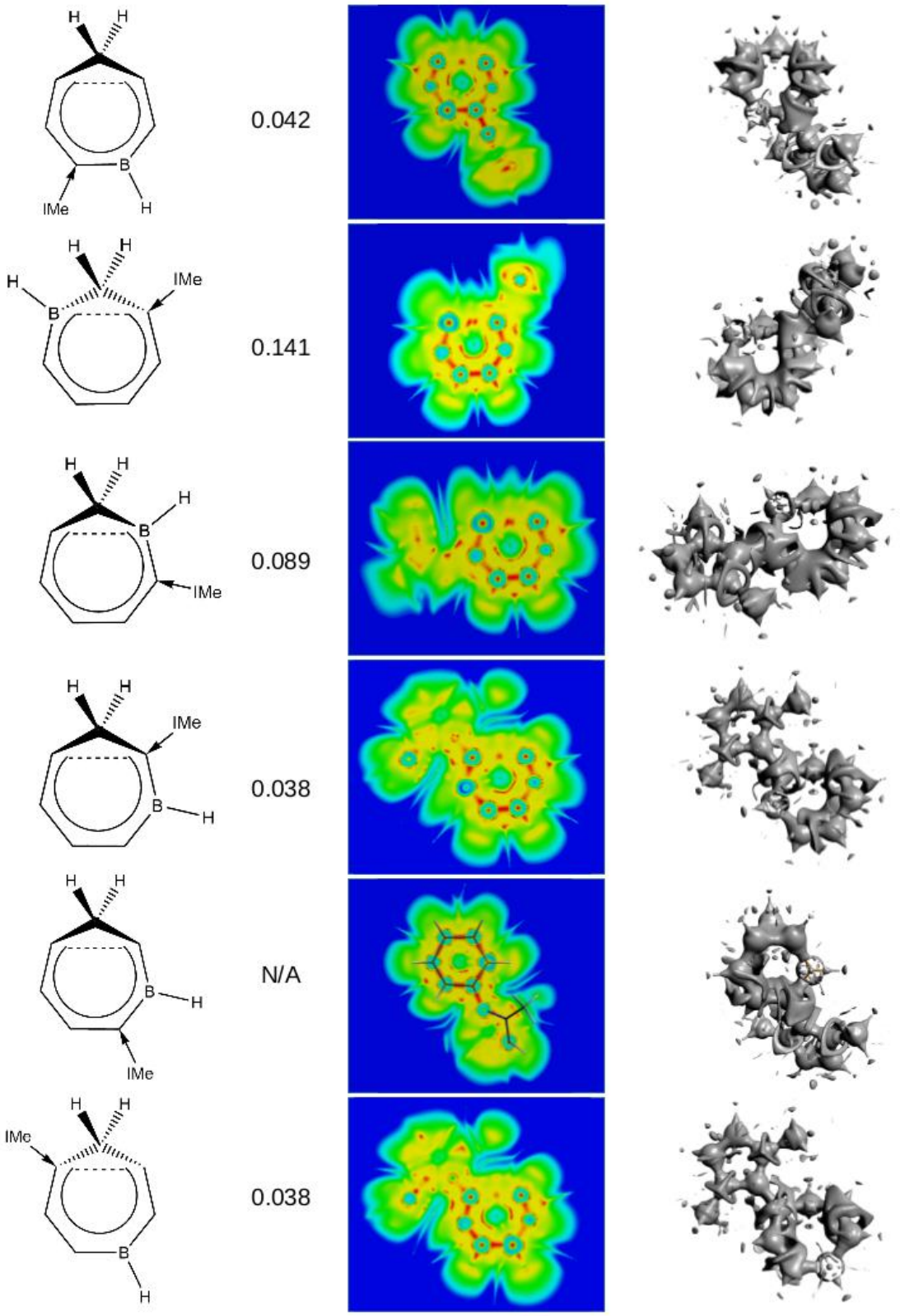

Figure 3: Contour planes and isosurfaces for a set of structural isomers of seven-membered homoaromatic candidates with IMe as a two-electron donor calculated with a QZ4P STO basis set. All isomers listed with their associated WBI bond orders.

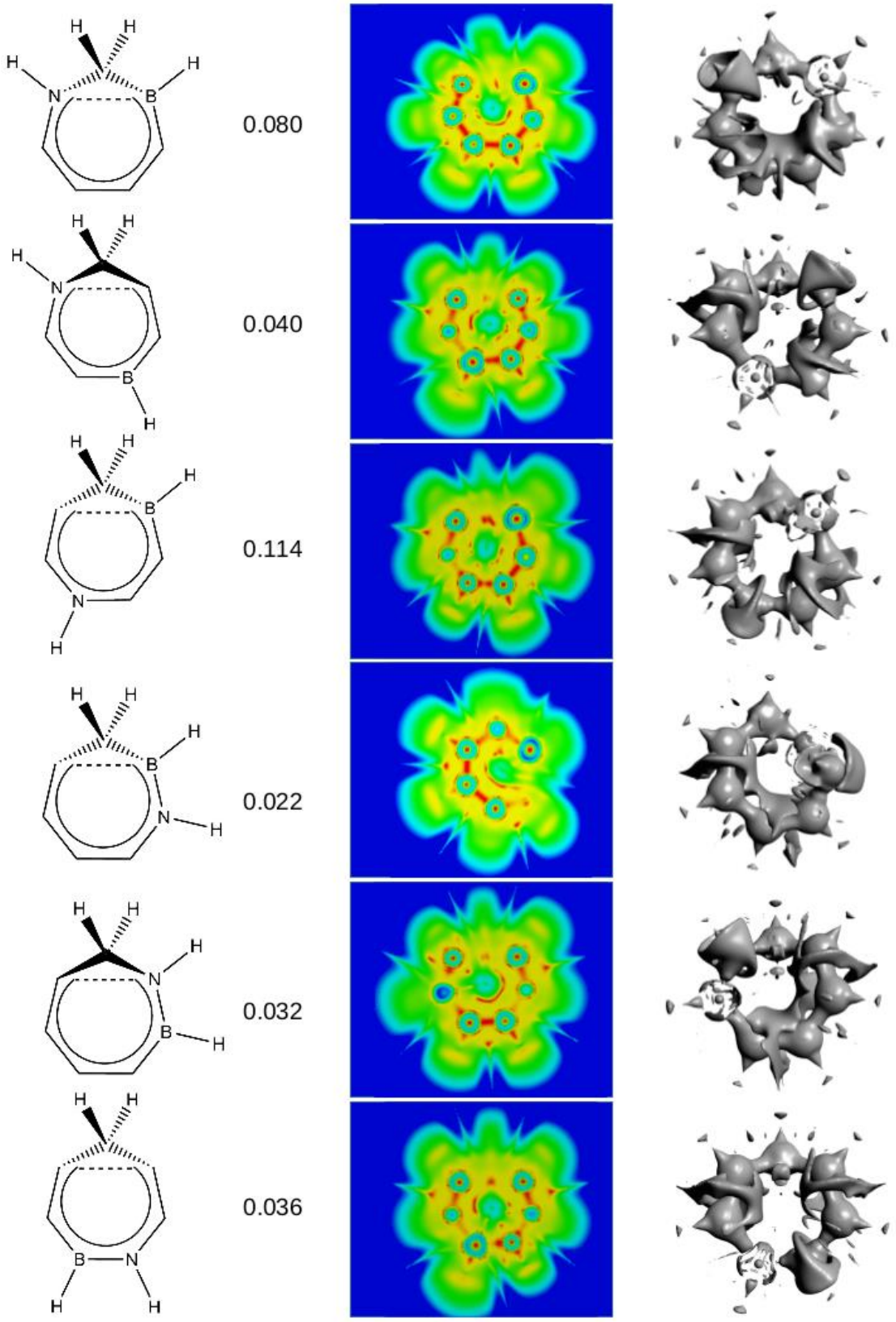

Figure 4: Contour planes and isosurfaces for a set of structural isomers of seven-membered homoaromatic candidates with a [N-H] fragment replacing the NHC as a two-electron donor calculated with a QZ4P STO basis set. All isomers listed with their associated WBI bond orders.

Although immediately obvious when viewing the geometry, figure 3 clearly shows that one of the isomers has rearranged, here the σ-bonding system can be seen to extend between all atoms in addition to the lack of any internal structure between the areas of electron density thus showing no evidence of aromaticity. This adds to the utility of the use of SEDD as a metric where through-space interactions of a large magnitude can cause significant bond-shortening, the lack of σ-bonding character could help confirm the presence of a homoaromatic interaction. Inspection of the contour planes for the remaining isomers reveals similar structures of near continuous arcs of electron density within the centre of the postulated homoaromatic systems. From the contour planes alone it is difficult to assess whether the variation of continuity results from a weakening or even the absence of the homoaromatic interaction or from a deviation away from planarity as discussed previously. Therefore the isosurfaces again prove more reliable in showing the homoaromatic interaction via the presence of the delocalized domains. The domains spread over all connected donor atoms in the system suggesting aromatic behaviour, furthermore, some part of the fragmentation of the delocalised isosurface is likely to be due to the deviation away from planarity that is common across the isomers. This behaviour of the isosurface could suggest that the variation of the homoaromatic interaction between structural isomers could be attributed to the variation in planarity of the compounds as much as the differing electronics caused by the spatial arrangement of the donor atoms. These effects should be expected to be co-dependent i.e. the incremental removal of electron density from the ring via a distortion away from the plane of the π-interaction will result in a weaker interaction. Both the contour planes and the isosurfaces show the correlated 'lobe' of electron density in the centre of the predicted through-space interaction. The degree of fragmentation of the delocalized domain may allow for a relative assessment of the strength of the interaction but this assessment obviously remains qualitative in nature.

It is also evident from both the contour planes and the isosurfaces that SEDD displays the 'electron deficient' nature of boron. This appears as areas of low electron density in the contour planes and as an absence of isosurface covering the core of the atom. Such behaviour is not observed with the carbocation centres in the early compounds. As both the [B-H] fragment and the carbocation should be isolobal this suggests significant delocalisation of the charge around the homoaromatic system. Whilst there is no delocalized domain present in the vicinity of the boron, the majority of the isomers still show some degree of homoaromatic interaction suggesting evidence for the electron 'sink' behaviour of boron allowing it to act as a charge redirection node.

Figure 4 displays the contour planes and isosurfaces for a set of structural isomers for a 7-membered ring including a boron centre and a [N-H] fragment acting as a two-electron donor in place of an NHC. Across this set of isomers there is generally an increase in the degree of fragmentation of the localization domain suggesting that the interaction is more likely to be more the result of conjugation rather than aromaticity in some of the isomers, however most of the structural isomers display a significant amount of through-space interaction suggesting that the addition of the boron atom is sufficient to maintain the homoaromatic interaction despite the introduction of a weaker donor.

Conclusions

Through the incremental modification of a set of previously identified homoaromatic candidates, both in the predictive and descriptive angles made possible by calculations based on DFT, it has been shown that boron can stabilize the homoaromatic interaction to a greater extent and with more control than the isolobal carbocation and that this stabilization is sufficient to allow the use of two-electron nitrogen donors to achieve a strong interaction across the homoconjugative gap. With this additional control it is then possible to introduce functionalization without compromising stability. The functionalization of neutral homoaromatic compounds theoretically allows for their insertion into useful systems in place of any other aromatic system when a perturbation to the strength of aromaticity would allow for a subtle modification towards desirable properties. Given the complexity in determining the properties inherent to homoaromatic compounds having a powerful and relatively computationally inexpensive method of electron localization is a useful addition to the theoretician's toolbox. SEDD identifies the presence of a through space interaction and the homoaromatic candidates identified previously display the 'fingerprints of aromaticity' as determined by de Silva et al. in literature and, more importantly, can clearly show a distinction between a homoaromatic interaction and mere conjugation. It is also apparent that SEDD will identify electron deficiency within a system and account for charge transferal across a boron node and thus would be of use showing a visible distinction between 6- and 8-electron boron. We thus have demonstrated a possible exploitation of boron's unique ability to act as a labile charge flux conveyance node.

Experimental Section

Geometry optimizations were performed using the Gaussian G09 software at the B3LYP/6-311G* level of theory with frequency calculations used to confirm a minima.[15] NMR[16] and NBO[17] calculations were performed at the same level of theory. It should be noted that, despite the through-space interaction being investigated, it was found that the use of additive dispersion term Grimme-D3 with BJ damping was found to be unnecessary in previous work and hence has not been included here. Additional optimizations were performed in the ADF programme at both the B3LYP/TZ2P and B3LYP/ZORA-QZ4P levels.[18] These were then used to perform SEDD calculations with a fine grid which were visualised within the ADF-GUI. Minima were confirmed by performing analytical frequency calculations. As suggested within existing literature, as the SEDD values can take any real value, they have been limited such that values below 2 are dark blue and those above 15 are red. The isosurfaces in this paper were generated using an isovalue of 5.0.[19] Using a QZ4P basis set also requires the use of a Zeroth Order Regular Approximation (ZORA) Relativistic Hamiltonian. See ESI for further details.

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Keywords: homoaromaticity • computational chemistry • DFT • boron • SEDD

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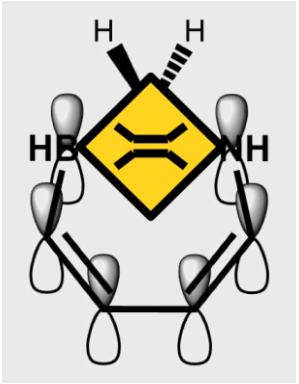
Layout 1:

ARTICLE

Homoaromatics, a step towards utility. Calculations show that homoaromatic interaction can be maintained whilst adding functionality through a combination of boron centres and two-electron donors. A confirmation of the interaction is shown using SEDD; an electron localization method.



*James D. Mattock, Alfredo Vargas**

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Boron centres allow design, control and systematic tuning of neutral homoaromatics for functionalization purposes

Layout 2:

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